

VLE Measurements and Modeling for Asymmetric Mixtures of Hydrocarbons

Mark C. Thies* and Doreen Thiele
Clemson University
Department of Chemical Engineering
Clemson, SC 29634-0909
Tele: (864) 656-5424; Fax: (864) 656-0784
mcths@clemson.edu
Grant No. DE-FG2601-NT41293
Sept 1, 2002 - present

Understanding and being able to predict the phase behavior of asymmetric mixtures of hydrocarbons (AMoHs), that is, mixtures of short- and long-chain alkanes, is of importance for a number of energy-related applications. Consider, for example, the operation of the Fischer-Tropsch (F-T) slurry bubble column (SBC) reactor, a key component in the conversion of coal to clean-burning liquid fuels. Attempts to accurately describe the phase behavior in this reactor have met with only limited success, primarily because of the lack of experimental data needed for model development. Vapor-liquid equilibrium (VLE) measurements for AMoHs are scarce, particularly for systems containing alkanes $>C_{20}$ in length. The data that are available suggest that both cubic (e.g., Peng-Robinson) and modern, fundamentally based equations of state (e.g., SAFT) are potentially useful tools, but the data are simply too limited to draw definitive conclusions.

Therefore, comprehensive VLE measurements are being carried out for binary mixtures of short- (e.g., C_2 - C_4) and long-chain (e.g., C_{16} - C_{44}) *n*-alkanes at temperatures to 300 °C and pressures to the mixture critical point of the binary system of interest. Currently, VLE measurements are being performed for the propane ($T_c = 96.6$ °C, $P_c = 42.5$ bar)/hexadecane ($T_c = 449$ °C, $P_c = 14.1$ bar) system at temperatures from 200 to 350 °C. Results indicate that the two-phase region for this binary mixture extends all the way to pressures exceeding 100 bar; clearly one cannot assume that the maximum two-phase pressure exhibits linear behavior between the two pure component critical pressures, usually a reasonable assumption for similarly sized hydrocarbons. In addition, the hexadecane is quite soluble in the gas phase at conditions corresponding to those that would exist in the F-T reactor; for example, at 20 bar and 300 °C, the solubility of hexadecane in the gas phase is almost 10 mol %.

A separation method known as dense-gas extraction (DGE) is being evaluated for the isolation of relatively pure higher molecular (MW) weight (i.e., $>C_{44}$) alkanes in g-sized quantities that could serve as MW standards for Fischer-Tropsch waxes. Such standards would also be used to obtain much needed VLE measurements for highly asymmetric mixtures of hydrocarbons. A preliminary design of our DGE apparatus has been used to isolate a ~90% pure cut with a molecular weight of about 350 (corresponding to $\sim C_{25}H_{52}$), so we are encouraged with the potential of this separation technique.